

KOKAI PATENT APPLICATION NO. HEI 3-31309

JAPANESE PATENT OFFICE (JP)

PATENT JOURNAL (A)

KOKAI PATENT APPLICATION NO. HEI 3-31309

Int. Cl.<sup>5</sup>:

C 08 F      220/22  
              220/30  
G 02 B      1/04  
//C 09 J      4/02

Identification code:

MMS A  
MMV B  
MMN  
JBL

Sequence Nos. for Office Use:

8620-4J  
8620-4J  
8620-4J  
7102-2H  
8620-4J

Application No.:

Hei 1-164798

Application Date:

June 27, 1989

Publication Date:

February 12, 1991

No. of Inventions:

1 (Total of 7 pages)

Examination Request:

Not requested

A COMPOSITION USED FOR PRODUCTION OF A RESIN WITH A HIGH REFRACTIVE INDEX

[*Kohkussetsuritsu jyushi sakuseiyoh soseibutsu*]

KOKAI PATENT APPLICATION NO. HEI 3-31309

Applicant:

Matsushita Electric Co.  
1048 banchi, Kadoma  
Oaza, Kadoma-shi  
Osaka-fu

Inventors:

Kohhei Onodera  
c/o Matsushita Electric Co.  
1048 banchi, Kadoma  
Oaza, Kadoma-shi  
Osaka-fu

Kohji Takagi  
c/o Matsushita Electric Co.  
1048 banchi, Kadoma  
Oaza, Kadoma-shi  
Osaka-fu

Shin'ichi Iketani  
c/o Matsushita Electric Co.  
1048 banchi, Kadoma  
Oaza, Kadoma-shi  
Osaka-fu

Agent:

Takehiko Matsumoto  
Patent attorney

*[There are no amendments to this patent.]*

*[In this translation, product names are spelled phonetically.]*

## Specification

### 1. Title of the invention

A composition used for production of a resin with a high refractive index

### 2. Claims of the invention

1. A composition used for production of a resin with a high refractive index wherein a composition containing three types of monomers of (A), (B) and (C) below at the mixing ratios shown for the total of the above-mentioned three monomers is used as a monomer.
  - (A) 40~60 % by weight of (meth)acrylate having a halogenated aromatic ring,
  - (B) 5~35 % by weight of polyhydric (meth)acrylate having an aromatic ring and
  - (C) 15~35 % by weight of a monohydric (meth)acrylate having an aromatic ring.

### 3. Detailed description of the invention

#### [Field of industrial application]

The present invention pertains to a composition used for production of a resin with a high refractive index suitable to be used as a sealer for applications where transparency is required such as the core material of an optical fiber, an adhesive for connection of optical fibers, adhesive for optical glasses, optical lenses, photo diodes, etc.

#### [Prior art]

An optical circuit board (planar optical waveguide) is used inside optical devices used for optical measurements and sensing to guide the light from the external optical system to the light

receiving element or to guide the light emitted from a luminous element to an external optical system.

For the above-mentioned optical circuit board, those made of materials such as semiconductor crystals, dielectric crystals, glass and plastic have been suggested.

For production of an optical circuit board made of a plastic resin, a method is known wherein a plastic resin is poured into a die to produce a resin substrate having a waveguide portion or lattice portion curved to form a recess, a plastic resin with a high refractive index is poured into the above-mentioned waveguide portion or lattice portion and excess resin is scrapped off the resin substrate (Japanese Kokai [Unexamined] Patent Application No. Sho 63-139304).

[p. 2]

For the material used for formation of the above-mentioned substrate for the optical circuit board, thermoplastic resins, thermosetting resins, photo-curable resins, etc. can be mentioned. For the material used for production of the core material, a resin having three characteristics: (1) high refractive index, (2) a lower reduction of transparency with time, and (3) strong adhesion to other resins is desirable.

[Problems to be solved by the invention]

In the past, monomers containing a benzene ring or monomers containing a halogen (with the exception of fluorine) have been used as monomers capable of achieving a high refractive index, at times. However, the refractive index is not sufficient when a monomer containing benzene alone is used, and adhesion with other resins or substrates is not adequate when a monomer containing a halogen alone is used; furthermore, handling is difficult when a solid

monomer is used. In order to compensate for the above-mentioned disadvantages of the above monomers, mixing of a monomer containing benzene and a monomer containing halogen has been used in practice, but whitening occurs when used under high temperature and high humidity conditions and practical application is not possible.

The objective of the present invention is to produce a composition used for production of a resin with high refractive index for production of a resin having the above-mentioned three properties: (1) high refractive index  $n//illegible^1// = 1.57$  or higher), (2) lesser reduction in transparency with time, and (3) high adhesion with other resins.

[Means to solve the problem]

In the present invention, in order to eliminate the above-mentioned existing problems, a composition used for production of a resin with a high refractive index wherein a composition containing three types of monomers of (A), (B) and (C) below at the mixing ratios shown for the total of the above-mentioned three monomers is used as a monomer.

- (A) 40~60 % by weight of (meth)acrylate having a halogenated aromatic ring,
- (B) 5~35 % by weight of polyhydric (meth)acrylate having an aromatic ring and
- (C) 15~35 % by weight of a monohydric (meth)acrylate having an aromatic ring, is used.

Monomer (A) used in the present invention is a monomer mainly used for imparting a high refractive index, and is a (meth)acrylate having a halogenated aromatic ring. For the above-mentioned (meth)acrylate, one or a mixture of at least two compounds represented by structural formulas [A1] and [A2] below are desirable. The (meth)acrylate shown in structural formula

---

<sup>1</sup>Translator's note: subscript and exponent illegible due to poor copy quality of source document.

[A1] is a (meth)acrylate having bisphenol A as the main skeleton, and the two benzene rings are brominated and have ethylene oxide or hydroxyethylene oxide with 0~3 repeating units as a side chain of the benzene ring. The (meth)acrylate shown in structural formula [A2] below is a (meth)acrylate having phenol as the main skeleton, and the benzene ring is brominated and has ethylene oxide or hydroxyethylene oxide with 0~3 repeating units as a side chain of the benzene ring. When the repeating units of the above-mentioned ethylene oxide or hydroxyethylene oxide exceed 3 per side chain, a reduction in adhesion and a reduction in refractive index results; thus, it is not suitable for the above-mentioned applications. In this case, it is necessary for the mixing ratio of monomer (A) to be in the range of 40~60 % by weight for the total monomer. When the above-mentioned ratio is less than 40 % by weight, the refractive index is not adequate, and when greater than 60 % by weight the adhesion is not adequate and the above-mentioned purpose cannot be achieved. In order to achieve the above purpose, a (meth)acrylate having a brominated aromatic ring is suitable for monomer (A) but those having an aromatic ring where the hydrogen atom is replaced with a halogen other than bromine (with the exception of fluorine) can be used as well.

The monomer (B) used in the present invention is a monomer mainly used for formation of a higher-order matrix and is a polyhydric (meth)acrylate having an aromatic ring. For the above-mentioned (meth)acrylate, for example, a polyhydric (meth)acrylate having bisphenol A as the main skeleton or a polyhydric epoxy (meth)acrylate is suitable, and one or a mixture of at least two compounds shown in structural formula [B1] shown below is desirable. The (meth)acrylate shown in the structural formula [B1] below is a divalent (meth)acrylate having bisphenol A as the main skeleton and further having an ethylene oxide or a hydroxyethylene

oxide with 0~3 repeating units per side chain as a side chain of the bisphenol A skeleton.

[p. 3]

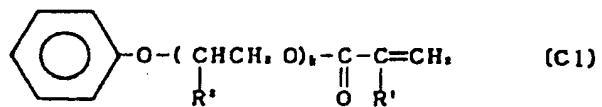
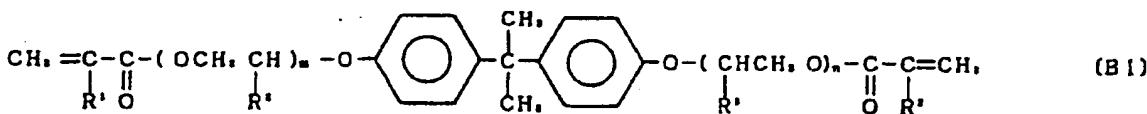
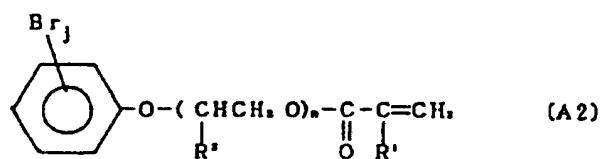
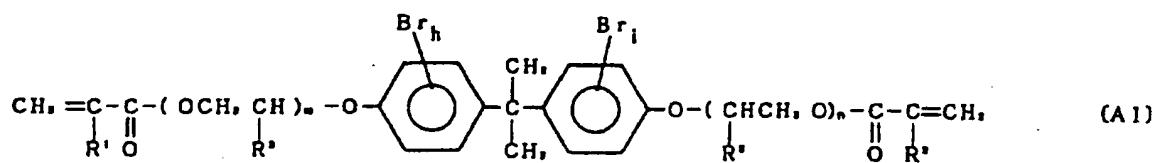
When the repeating units of the above-mentioned ethylene oxide or hydroxyethylene oxide exceed 3 per side chain, the viscosity of the monomer mixture is increased significantly, and practical application is not possible. In this case, it is necessary for the mixing ratio of monomer (B) to be in the range of 5~35 % by weight for the total monomer. When the above-mentioned ratio is 5 % by weight or below, adhesion is not adequate and when 35 % by weight or above, whitening occurs when used under high temperatures and high humidity and practical application is not possible. The above purpose cannot be achieved.

Monomer (C) used in the present invention is a monomer that is mainly used for reducing the viscosity of the monomer mix, and is a monovalent (meth)acrylate having an aromatic ring. For the above-mentioned (meth)acrylate, for example, a monomer with a low molecular weight is suitable, and one or a mixture of two at least compounds represented by structural formula [C1] shown below is desirable. The (meth)acrylate shown in structural formula [C1] below is a monovalent (meth)acrylate having an ethylene oxide or a hydroxyethylene oxide with 0~2 repeating units per side chain as a side chain of the benzene ring. When the above-mentioned repeating units exceed 2, the viscosity is increased, and the dilution effect is not significant, and a reduction in adhesion, reduction in refractive index, and whitening are conceivable when used at high temperatures and high humidities, and practical application is not possible. In this case, it is necessary for the mixing ratio of the monomer (C) to be in the range of 15~35 % by weight for the total monomer. When the above-mentioned ratio is less than 15 % by weight, the viscosity of

the monomer mixture is increased and when greater than 35 % by weight, a reduction in the refractive index results.

The above-mentioned monomers (A), (B) and (C) may include aromatic rings other than benzene rings.

It is not necessary to use only one of each type of the above-mentioned monomers, and a combination of monomers can be used for each monomer type, as well.



[Wherein, R<sup>1</sup> and R<sup>2</sup> each represent H or CH<sub>2</sub>, R<sup>3</sup> is H or OH, m and n are each 0~3, h and i are each 1~2, j is 1~3, and k is 0~2]

[p. 4]

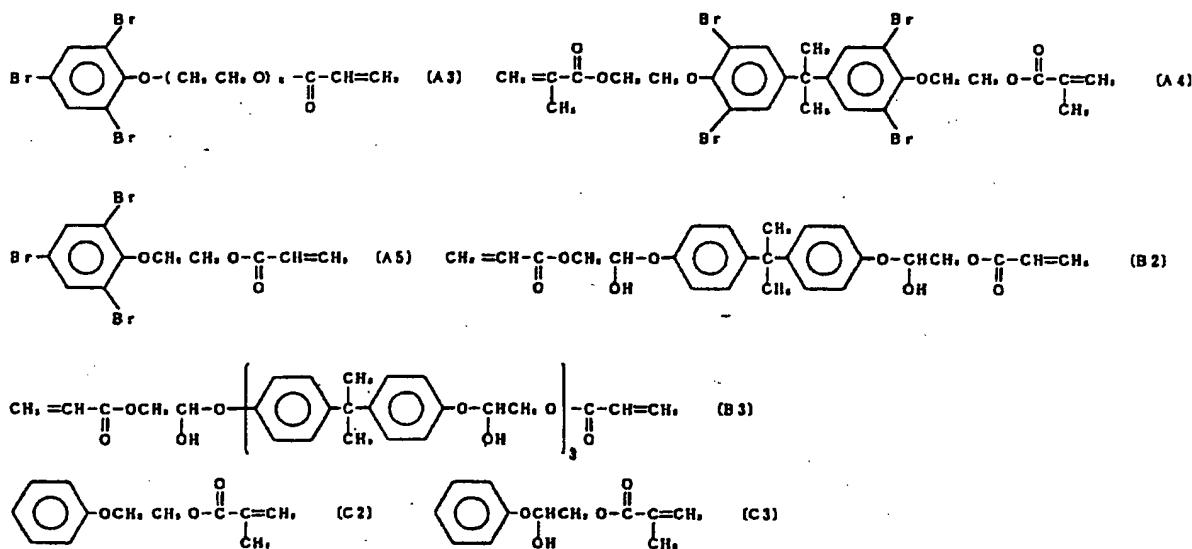
For the curing method used for the resin, for example, photopolymerization can be mentioned. In which case, a photopolymerization initiator is added. The photopolymerization

initiators that can be used in this case are not especially limited, and either acetophenones or benzophenones are suitable from the standpoint of a lower degree of coloring after curing, and the amount used is in the range of 0.5~5 % by weight for 100 % by weight of the monomer. As for the method of application of the light, it is not especially limited, and a standard ultra-high pressure mercury lamp, etc. can be used in this case.

The method used for mixing is not especially limited as long as a uniform mixing can be achieved.

#### [Application Examples]

In the following, specific application examples of the present invention, comparative examples and examples of the prior art are shown, but the present invention is not limited to these examples. Structural formulas of the monomers used in the following application examples of the present invention, comparative examples, and examples of the prior art are listed below.



[p. 5]

Monomers [A3], [A4] and [A5] with the structural formulas shown on the previous page [of source document] are monomers mainly used for imparting a high refractive index, monomers [B2] and [B3] are monomers mainly used for formation of a higher-order matrix, and monomers [C2] and [C3] are monomers mainly used for dilution.

#### -Application Example 1-

Mixing was carried out for monomers to form the compositions shown in Table I below. Subsequently, 1 % by weight of Daro-cure 1116 (product of Ciba Geigy Corporation) was added for the above-mentioned monomer composition to produce a composition used for production of a resin with high refractive index. As shown in Fig. 1, the above-mentioned composition used for production of a resin with high refractive index was injected into the hole of spacer 3 (thickness of 1 mm) made of silicone rubber produced ahead of time by a laser and placed on substrate 2 made of 2-methyl pentene, being careful so as not to include air bubbles,

and a cover consisting of a PET film 4 with a thickness of 25  $\mu\text{m}$  was applied. Then, UV rays (wavelength of 325 nm) of 5000 mJ/cm<sup>2</sup> were applied to the above-mentioned molding from the direction indicated by the arrow at an intensity of 4 mW/cm<sup>2</sup> and curing was carried out for the composition used for production of a resin with high refractive index.

-Application Examples 2~6-

In Application Example 1 above, the composition of the monomer mixture was changed as shown in Table I and mixing of the monomers was done as in Application Example 1, a photopolymerization initiator was added and curing of the composition used for production of a resin with high refractive index was carried out as explained above.

-Comparative Examples 1~8-

In Application Example 1 above, a composition was used for the monomer mixture that is outside the range of the present invention as shown in Table I and mixing of the monomers was carried out as in the case of Application Example 1, a photopolymerization initiator was added and curing of the composition used for production of a resin with high refractive index was carried out as explained above.

-Example of the Prior Art 1-

The monomer mixture of prior art used for production of a resin with a high refractive index shown in Table I was used and a photopolymerization initiator was added and curing of the composition used for production of a resin with high refractive index was carried out as in Application Example 1.

For the monomer mixtures or hardened materials produced in the above-mentioned application examples of the present invention, comparative examples, and example of the prior

art, the evaluations shown below were performed.

(1) Viscosity test of the monomer mixture

The viscosity of the monomer mixture was measured at a temperature of 25EC using an E-type viscometer upon adjusting the rotational speed of the rotor to 100 or 50 rpm.

(2) Transparency (degree of whitening) after boiling

An alumina powder with a particle diameter of 0.3  $\mu\text{m}$  was used as an abrasive powder and polishing was performed for the surface of the hardened material so as to form a uniform surface. The above-mentioned test piece was cut to form a size of 20 mm x 20 mm, dipped in boiling water for 30 minutes, and rapid cooling was performed under running water and the transparency was visually examined on a black paper with a matte surface and a classification into 5 grades from 1 to 5 was carried out (in this case, the higher the number, the greater the transparency).

(3) Adhesion test of hardened material

A hole with a diameter of 2 mm was punched in spacer 3 made of a silicone rubber with a thickness of 1 mm, and an acrylic sheet was used as the substrate and curing of the composition used for production of a resin with high refractive index was carried out as in the case of Application Example 1 above. The PET film 4 and silicone rubber spacer 3 were removed after curing, and the adhesive strength of the hardened material was measured by a Push-Pull gage.

(4) Refractive index of the hardened material

The hardened material produced by the method described in Application Example 1 was cut to a size of 10 mm x 20 mm and polishing was performed for the cut surface with an alumina powder having a particle diameter of 0.3  $\mu\text{m}$ , and measurement was performed for the refractive

index of the hardened material with an Abbe refractometer ( $n$ //*illegible*//).

The results obtained above are shown in Table I below.

[p. 6]

Table I

	Monomers used for production of the composition used in production of the resin with high refractive index (% by weight)					Viscosity of the monomer mixture (cps)	Properties of hardened material				
	Monomer [A3]	Monomer [A4]	Monomer [B2]	Monomer [B3]	Monomer [C2]		Monomer [C3]	Transparency	Adhesive strength (kg/cm <sup>2</sup> )	Refractive index	
Application Example 1	35	15	XXX	10	10	30	XXX	400	3	95	1.581
Application Example 2	50	XXX	XXX	20	XXX	15	15	210	4	235	1.577
Application Example 3	35	15	XXX	20	XXX	20	10	275	5	145	1.582
Application Example 4	42.5	7.5	XXX	25	XXX	15	10	700	5	260	1.581
Application Example 5	45	5	XXX	30	XXX	20	XXX	720	5	80	1.582
Application Example 6	XXX	15	35	10	10	30	XXX	500	3	95	1.582
Comparative Example 1	100	XXX	XXX	XXX	XXX	XXX	XXX	Paste	1	125*	1.627
Comparative Example 2	XXX	100	XXX	XXX	XXX	XXX	XXX	Solid	1	55*	1.623
Comparative Example 3	XXX	XXX	XXX	100	XXX	XXX	XXX	1,000,000	2	70*	1.567
Comparative Example 4	XXX	XXX	XXX	XXX	XXX	100	XXX	4	4	75	1.560
Comparative Example 5	XXX	XXX	XXX	XXX	XXX	100	180	1	1	310	1.550
Comparative	XXX	30	XXX	30	XXX	40	XXX	410	2	60	1.576

<b>Example 6</b>													
<b>Comparative Example 7</b>	50	15	XXX	5	XXX	20	10	90	1	90			1.584
<b>Comparative Example 8</b>	20	20	XXX	40	XXX	20	XXX	2500	1	65			1.579
<b>Prior Art Example 1</b>	XXX	50	XXX	XXX	XXX	XXX	50	250	1	80			1.586

- \* Cut with [C2] so that measurement was possible

[A3], [A4], or [B2]/[C2]=3/1

As shown in Table I above, a resin produced by curing the composition used for production of a resin with high refractive index having the monomer composition of the present invention is an excellent resin having (1) high refractive index ( $n_{//illegible//} = 1.57$  or higher), (2) lesser reduction of transparency with time, and (3) high adhesion with other resins.

Furthermore, a resin made of a monomer composition outside the range of the present invention lacks at least one of the above-mentioned properties.

#### [Effect of the invention]

The composition used for production of a resin with high refractive index of the present invention includes the above-mentioned specific monomers mixed at the specified ratios. Thus, when curing is carried out for the composition of the present invention, it is possible to produce an excellent resin having (1) high refractive index ( $n_{//illegible//} = 1.57$  or higher), (2) lower reduction in transparency with time, and (3) high adhesion with other resins.

#### 4. Brief description of figures

Fig. 1 is an explanatory drawing of an example of curing of the composition used for production of the resin with high refractive index of the present invention.

1 ... composition used for production of resin with high refractive index

Agent: Takehiko Matsumoto, patent attorney

[Fig. 1]

